



## Chemical


SAFETY AND SECURITY TRAINING

### Process Safety Overview

SAND No. 2011-0548P

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.





## Key acronyms


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**PSM** = *process safety management*

**SDS** = *safety data sheet*

**RAGAGEPS** = *recognized and generally accepted good engineering practices*

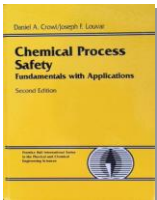








## Process safety resources

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**D.A. Crowl and J.F. Louvar 2001. *Chemical Process Safety: Fundamentals with Applications, 2nd Ed.*** Upper Saddle River, NJ: Prentice Hall.



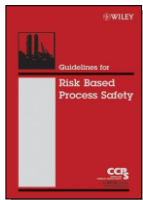







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**CCPS 2007a. Center for Chemical Process Safety, *Guidelines for Risk Based Process Safety***, NY: American Institute of Chemical Engineers.





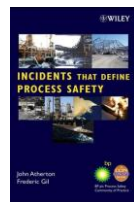
## Process safety resources

**CCPS 2008a.** Center for Chemical Process Safety, *Guidelines for Hazard Evaluation Procedures, Third Edition*, NY: American Institute of Chemical Engineers.



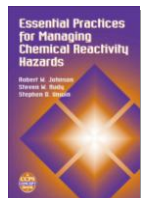
## Process safety resources

**CCPS 2008b.** Center for Chemical Process Safety, *Incidents that Define Process Safety*, NY: American Institute of Chemical Engineers.



## Process safety resources

**Johnson et al. 2003.** *Essential Practices for Managing Chemical Reactivity Hazards*, NY: American Institute of Chemical Engineers, accessible free after registration on [www.knovel.com](http://www.knovel.com).



## Process safety resources

**CCPS 2001.** Center for Chemical Process Safety, *“Reactive Material Hazards: What You Need To Know,”* NY: American Institute of Chem. Engineers, [www.aiche.org/uploadedFiles/CCPS/Resources/SafetyAlerts/reactmat.pdf](http://www.aiche.org/uploadedFiles/CCPS/Resources/SafetyAlerts/reactmat.pdf).





## Process Safety Overview

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1. What is *process safety*?
2. Opposite of process safety: Major incidents
3. The basic anatomy of process safety incidents
4. Overview of process safety strategies
5. Taking advantage of past experience
6. Defense in depth / layers of protection
7. Elements of process safety management



## Process Safety Overview

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1. What is *process safety*?



## Process safety

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**= the absence of loss and harm resulting from fires, explosions and hazardous material releases at process facilities.**

*(Event-focused definition)*



## Process safety

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**= the absence of loss and harm at process facilities by  
(a) identifying process hazards,  
(b) containing and controlling them,  
(c) countering abnormal situations with effective safeguards.**

*(Activity-focused definition)*




## Process Safety Overview

1. What is *process safety*?
2. Opposite of process safety: Major incidents




## Some major process incidents

- **Flixborough, UK (June 1974)**
  - Partial oxidation of cyclohexane
  - Catastrophic failure of temporary piping
  - 30 tonnes of hot cyclohexane released in 30 s
  - Vapor cloud explosion
  - 28 fatalities, 53 injuries; 1800+ houses damaged; plant destroyed
  - 18 of those fatally injured were in control room
  - Hastened passage of UK “Health and Safety at Work Act”

See CCPS 2008b for details of these incidents




## Some major process incidents

- **Seveso, Italy (July 1976)**
  - Runaway reaction
  - 2 kg of dioxin release from relief system
  - Over 17 km<sup>2</sup> affected
  - Locally grown food banned for several months
  - Several inches of topsoil removed, incinerated
  - 80,000 animals died or slaughtered
  - Plant shut down and destroyed
  - EU “Seveso Directive” prompted



## Some major process incidents

- **Mexico City, Mexico (November 1984)**
  - Large LPG / fuels storage facility
  - Fires, vessel ruptures, boiling-liquid-expanding-vapor explosions (BLEVEs)
  - Initiating cause unknown
  - 600 fatalities, 7000 injuries
  - Horizontal tanks rocketed as far as 1200 m away
  - Fixed fire protection destroyed by blasts
  - Fuels terminal destroyed



### Some major process incidents

#### •Bhopal, India (December 1984)

- Pesticide production facility
- Water introduced into methyl isocyanate storage
- MIC toxic vapor release from vent system
- 2000 to 3000 early fatalities; ~200,000 injuries
- Plant shut down; Union Carbide eventually sold
- Seveso II, EPA Risk Management Program prompted



### Some major process incidents

#### •Toulouse, France (September 2001)

- Ammonium nitrate storage at fertilizer plant
- Explosive decomposition initiated; cause unknown
- Equivalent blast energy 20-40 tons of TNT
- 30 fatalities; 2500+ injuries; US\$ 2 billion in losses




### Some major process incidents

#### •Texas City, Texas (March 2005)

- Refinery isomerization unit
- One valve not opened during unit re-start
- Release of hot flammable material from blowdown
- Ignition and vapor cloud explosion
- 15 fatalities, 170+ injuries; BP losses and impacts









## Some major process incidents

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- **Buncefield, UK (December 2005)**
  - Petrol (gasoline) tank farm
  - Storage tank overflow
  - Ignition, vapor cloud explosion and fires
  - 40+ injuries; 20+ tanks destroyed
  - Consequences could have been much worse

See [www.buncefieldinvestigation.gov.uk/index.htm](http://www.buncefieldinvestigation.gov.uk/index.htm) for details






## DISCUSSION

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When “major chemical incidents” is mentioned, what come first to your mind?




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## Process Safety Overview

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1. What is *process safety*?
2. Opposite of process safety: Major incidents
3. The basic anatomy of process safety incidents






## Process safety incident anatomy

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### Preface





This presentation is adapted from course materials and from presentations used for several years for process safety lectures at the University of Cincinnati and The Ohio State University, with updates to reflect terminology used in the Third Edition of *Guidelines for Hazard Evaluation Procedures* (CCPS 2008a).






## Incident - Definition

**Incident:**  
An unplanned event or sequence of events that either resulted in, or had the potential to result in, adverse impacts.






## Major process industry incidents

- Fires
- Explosions
- Toxic Releases




- Fatalities
- Injuries
- Environ. Damage
- Property Damage
- Evacuations
- Business Losses
- Plant Closings
- Fines, Lawsuits






## Major process industry incidents

**Loss Events**




- Fatalities
- Injuries
- Environ. Damage
- Property Damage
- Evacuations
- Business Losses
- Plant Closings
- Fines, Lawsuits





## Major process industry incidents

**Loss Events**



**Impacts**





## Key definition

### Loss event:

*Point of time in an abnormal situation when an irreversible physical event occurs that has the potential for loss and harm impacts.*

– CCPS 2008a Glossary



## Key definition

### Loss event:

*Point of time in an abnormal situation when an irreversible physical event occurs that has the potential for loss and harm impacts.*

– CCPS 2008a Glossary

#### Examples:

- Hazardous material release
- Flammable vapor or dust cloud ignition
- Tank or vessel overpressurization rupture



## Key questions

- **Why** do loss events happen?
- **How** do loss events happen?
- **What** must be done to avoid them?




## WHY do loss events happen?

- We choose to handle dangerous process materials and energies
  - To make a living
  - To provide society with desirable products
- As long as we choose to handle them, a potential for loss events exists




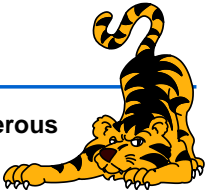






## Analogy




- We choose to handle dangerous animals at the Zoo
  - To make a living
  - To provide society with desirable experiences
- As long as we choose to handle them, a potential for loss events exists
  - Things can be done to reduce their likelihood and severity to negligible or tolerable levels



## Process safety




The absence of loss and harm at process facilities by

- (a) identifying process hazards,
- (b) containing and controlling them,
- (c) countering abnormal situations with effective safeguards.





## Process hazard - Definition

*Presence of a  
stored or connected  
material or energy with  
inherent characteristics  
having the potential for  
causing loss or harm.*



## Three types of process hazards

- Material hazards
- Energy hazards
- Chemical interaction hazards





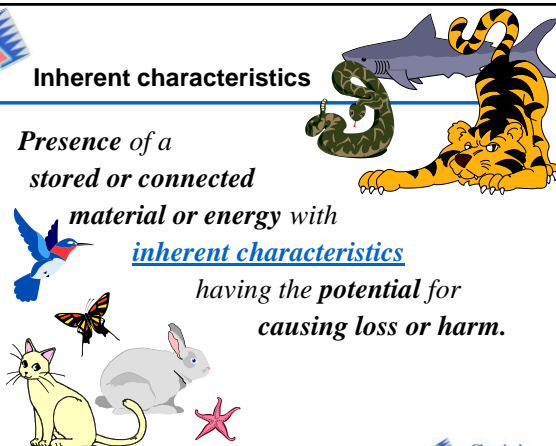
## Three types of process hazards

- **Material hazard:** A contained or connected process material with one or more hazardous characteristics
- Energy hazard
- Chemical interaction hazard



## Inherent characteristics

*Presence of a  
stored or connected  
material or energy with  
inherent characteristics  
having the **potential** for  
causing loss or harm.*



## Material hazards

### Inherently hazardous characteristics:



Flammability



Instability



Toxicity



Corrosivity

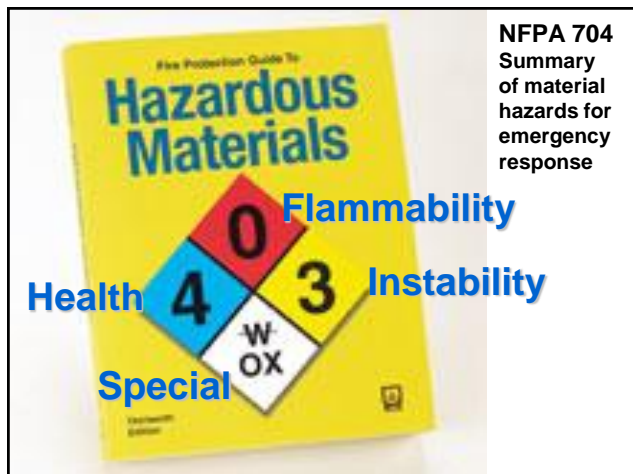


## E.g., Flammable/combustible materials



### Inherent characteristics:

- Flash point (volatility)
- Heat of combustion
- Ease of ignition
  - Flammability limits
  - Minimum ignition energy
  - Autoignition temperature



NFPA 704  
Summary  
of material  
hazards for  
emergency  
response

Flammability

Health

Special

Instability



## SDSs

### Safety Data Sheets

- More complete summary of hazards
- Required to be accessible in workplace
- All hazardous materials on-site
- Available from suppliers, internet sources
- Give only basic chemical reactivity info
- Often inconsistent from source to source



## Limitations


- NFPA 704 diamonds and SDSs only give properties of individual hazardous materials
  - Hazardous energies not identified
  - Some hazardous chemical interactions not identified
  - Connected hazards may not be identified



## Three types of process hazards


- **Material hazard**
- **Energy hazard:** Some form of physical energy contained within or connected to the process with the potential for loss or harm
- **Chemical interaction hazard**

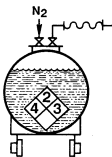






## Process hazard

**Presence of a**  
**stored or connected**  
**material or energy with**  
**inherent characteristics**  
**having the potential for**  
**causing loss or harm.**





*having the potential for*  
*causing loss or harm.*

Form of Energy with Injury Potential (examples)
Electrical (voltage, capacitance)
Mechanical (spring, machine parts)
Kinetic (moving or rotating mass)
Positional (elevated part or equipment)
Hydraulic (liquid under pressure)
Pneumatic (gas/vapor under pressure)
Chemical–Health Hazard (NFPA 2 to 4)
Chemical–Flammables (NFPA 3 or 4)
Chemical–Combustibles (NFPA 2)
Chemical–Reactive (NFPA 2 to 4)
Thermal–Hot Material (steam, hot oil)
Thermal–Cryogenic Fluid (liquid N <sub>2</sub> )

### LOCKOUT/TAGOUT ENERGY CONTROL PROCEDURE

Page 1 of 1

**Drawing No.** X-100-101

**Equipment Name** Methanol Flowmeter

**Location** Bldg 1, Inside dike wall

Form of Energy with Injury Potential (examples)	Connected Energy Source and Magnitude	Residual and/or Stored Energy?
Electrical (voltage, capacitance)		
Mechanical (spring, machine parts)		
Kinetic (moving or rotating mass)		
Positional (elevated part or equipment)		
Hydraulic (liquid under pressure)	MeOH pump discharge, 3 bar g	
Pneumatic (gas/vapor under pressure)		
Chemical–Health Hazard (NFPA 2 to 4)	MeOH, up to 10,000 liters	Yes
Chemical–Flammables (NFPA 3 or 4)	MeOH, up to 10,000 liters	Yes
Chemical–Combustibles (NFPA 2)		
Chemical–Reactive (NFPA 2 to 4)		
Thermal–Hot Material (steam, hot oil)		
Thermal–Cryogenic Fluid (liquid N <sub>2</sub> )		

**ISOLATE CONNECTED ENERGY SOURCES**

**Energy Isolating Device #1** Ball Valve

**Location** Between MeOH transfer pump and flowmeter

**Use of Device** Close valve

**LOTO** Lockout and tagout **Initials** \_\_\_\_\_

### LOCKOUT/TAGOUT ENERGY CONTROL PROCEDURE

Page 1 of 1

**Drawing No.** X-100-101

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**ISOLATE CONNECTED ENERGY SOURCES**

**Energy Isolating Device #1** Ball Valve

**Location** Between MeOH transfer pump and flowmeter

**Use of Device** Close valve

**LOTO** Lockout and tagout **Initials** \_\_\_\_\_

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**BLEED OFF RESIDUAL OR STORED ENERGIES**

**Bleed-Off Procedure:**  
 Drain residual flammable liquid into grounded catch pan.  
**Initials** \_\_\_\_\_

**VERIFY ISOLATION AND DEENERGIZATION**

**Verification Procedure:**  
 Visually check for pockets of flammable liquid while disassembling.  
**Initials** \_\_\_\_\_



## Three types of process hazards

- **Material hazard**
- **Energy hazard**
- **Chemical interaction hazard:**  
Presence of materials with the potential for loss or harm upon their interaction in an unintentional or uncontrolled manner



## Reactive interactions

Example Compatibility Chart for an Acetic Anhydride Handling Facility

Will These Two Materials React?	Acetic Acid	Acetic Anhydride	Cooling Water	Sulfuric Acid	50% Caustic	Lube Oil	Cleaning Solution
Acetic Acid							
Acetic Anhydride	Reactive						
Cooling Water	Not reactive	Reactive					
Concentrated Sulfuric Acid	Reactive	Reactive	Reactive				
50% Caustic	Reactive	Reactive	Reactive	Reactive			
Lube Oil	Not reactive	Not reactive	Not reactive	Reactive	Reactive		
Cleaning Solution	Find out what the cleaning solution contains, then determine reactions						

From CCPS 2001



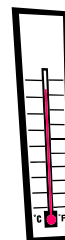
## Process hazard

*Presence of a stored or connected material or energy with inherent characteristics having the potential for causing loss or harm.*



## Degree of hazard

- **More hazardous material**  
→ **greater degree of hazard**
- **Farther from zero energy state**  
→ **greater degree of hazard**





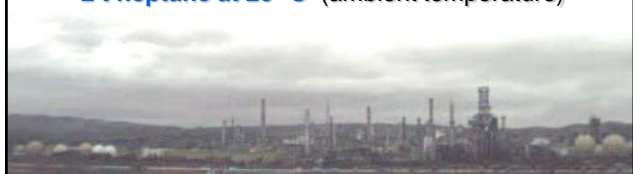
### EXERCISE

Which has more available energy?

1 t heptane at 98 °C

or

2 t heptane at 20 °C (ambient temperature)



### EXERCISE

1 t heptane, 98 °C

Chemical energy = 44,600 MJ

Thermal energy = 200 MJ

Total = 44,800 MJ

2 t heptane, ambient temperature

Chemical energy = 89,200 MJ

Thermal energy = 0 MJ

Total = 89,200 MJ



### Form of Energy with Injury Potential (examples)

Electrical (voltage, capacitance)

Mechanical (spring, machine parts)

Kinetic (moving or rotating mass)

Positional (elevated part or equipment)

Hydraulic (liquid under pressure)

Pneumatic (gas/vapor under pressure)

Chemical–Health Hazard (NFPA 2 to 4)

Chemical–Flammables (NFPA 3 or 4)

Chemical–Combustibles (NFPA 2)

Chemical–Reactive (NFPA 2 to 4)

Thermal–Hot Material (steam, hot oil)

Thermal–Cryogenic Fluid (liquid N<sub>2</sub>)

### Zero Energy State

0 volts

Sprung

At rest

Ground level

0 bar gage

0 barg, 0 m<sup>3</sup>

Nontoxic

Non-flammable

Nonreactive

Ambient

Ambient



### Key questions

- Why do loss events happen?
- How do loss events happen?
- What must be done to avoid them?





## HOW do loss events happen?

- Anatomy of an incident
- Unsafe act & condition precursors



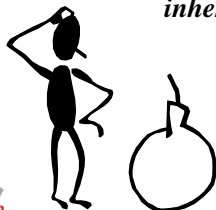
## Incident sequence: *Initiating cause*

- (Hazard)
- Cause
  - Deviation
  - Loss event
  - Impacts



## Process hazard


Presence of a  
stored or connected  
material or energy with  
inherent characteristics  
having the *potential* for  
causing loss or harm.



## Normal operation




During **normal operation**,  
all hazards are contained  
and controlled...






## Normal operation

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**Hazards**





During normal operation, all **hazards** are contained and controlled, **but they are still present.**

## Incident sequence: *Initiating cause*

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- (Hazard)
- **Cause**
  - Deviation
  - Loss event
  - Impacts





## Initiating cause

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Every incident starts with an **initiating cause** (also called an **initiating event** or just a “**cause**”).




**Hazards**



*Cause*

*Example initiating causes:*

- Feed pump fails off
- Procedural step omitted
- Truck runs into process piping
- Wrong raw material is received
- Extreme low ambient temperature






## Initiating cause



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Once an **initiating cause** occurs, normal operation cannot continue without a process or operational response.

**Hazards**



*Cause*





## Incident sequence: *Deviation*

- (Hazard)
- Cause
- **Deviation**
- Loss event
- Impacts



## Deviation

The immediate result of an initiating cause is a **deviation**.



Cause

### **Deviation**

- No Flow
- Low Temperature
- High Pressure
- Less Material Added
- Excess Impurities
- Transfer to Wrong Tank
- Loss of Containment
- etc.



## Abnormal situations

- Most engineering focuses on designing a process to **work**:  
(normal situation)
- We must also consider how a process can **fail**,  
starting with an  
“abnormal situation”



## Deviation


A **deviation** is an abnormal situation,  
outside defined design or operational parameters.



Cause

### **Deviation**



- No Flow
- Low Temperature
- **High Pressure** (exceed upper limit of normal range)
- Less Material Added
- Excess Impurities
- Transfer to Wrong Tank
- Loss of Containment
- etc.



## Incident sequence: *Loss event*

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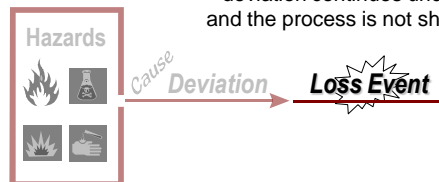
- (Hazard)
- Cause
- Deviation
- **Loss event**
- Impacts

## Loss event

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A **loss event** will result if a deviation continues uncorrected and the process is not shut down.



**Hazards**

*Cause* Deviation → **Loss Event**

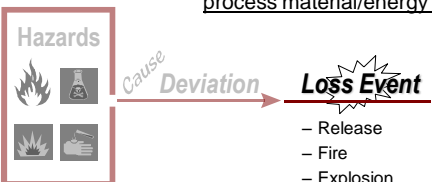
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## Loss event

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**Loss events** are generally irreversible process material/energy releases.




**Hazards**

*Cause* Deviation → **Loss Event**

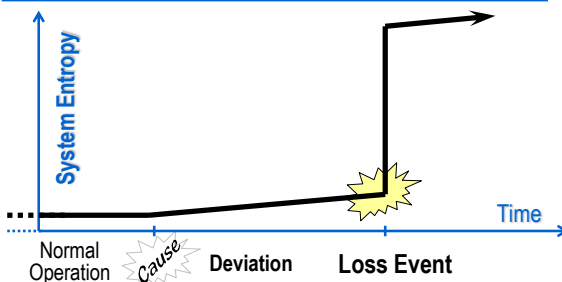
- Release
- Fire
- Explosion

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## Loss event: Step change in system entropy

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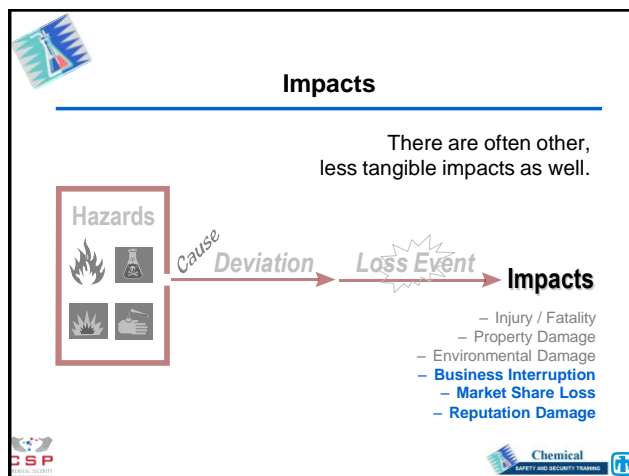
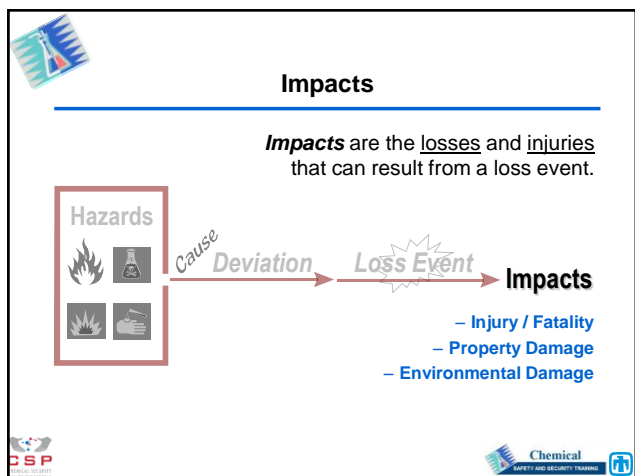
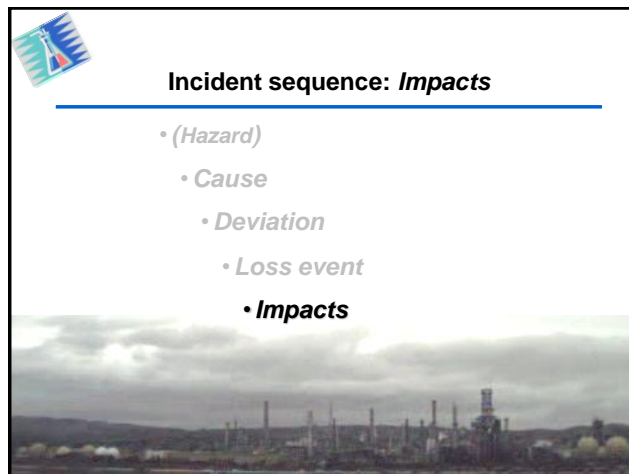
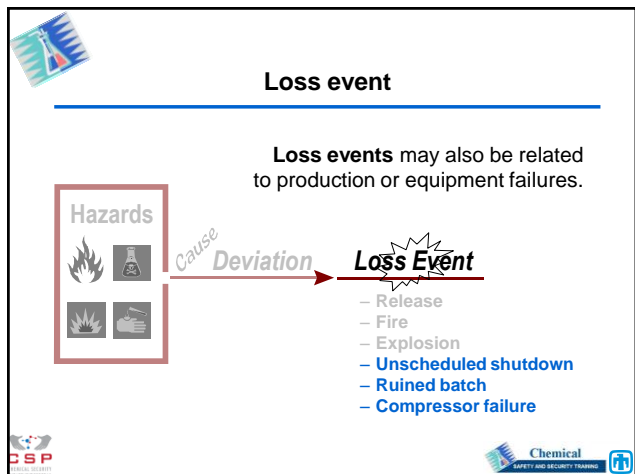
**System Entropy**

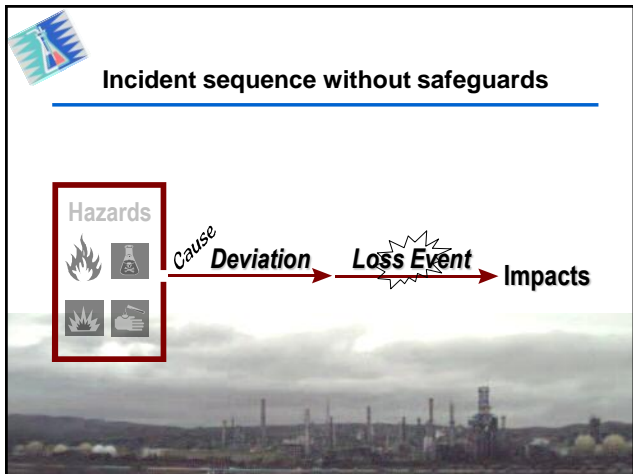
**Time**

Normal Operation → *Cause* Deviation → **Loss Event**

- Release
- Fire
- Explosion



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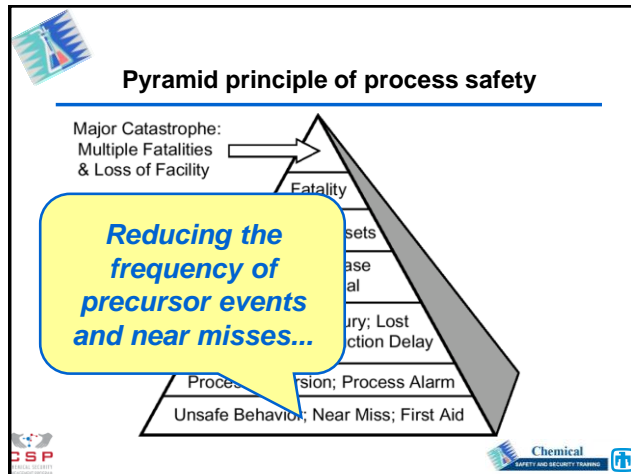
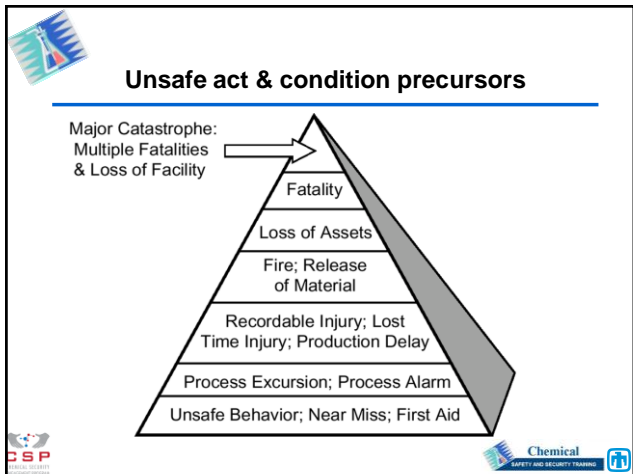


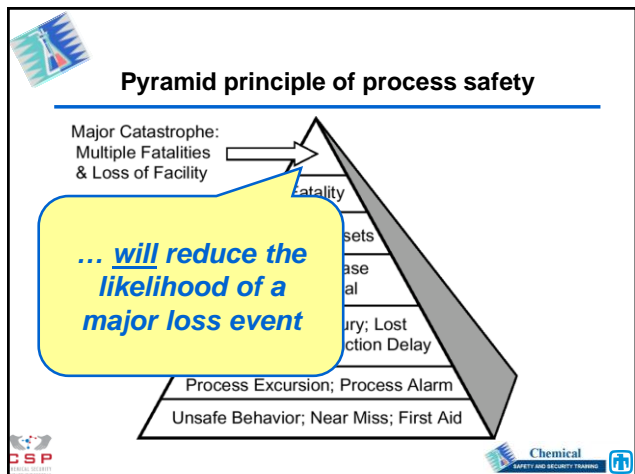


### HOW do loss events occur?

- Anatomy of an Incident
- Unsafe act & condition precursors





**Key questions**

- **Why** do loss events happen?
- **How** do loss events happen?
- **What** must be done to avoid loss events?

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*What must be done*

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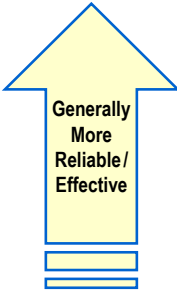
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## Overview of process safety strategies


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- **Inherent** - Hazard reduction
- **Passive** - Process or equipment design features that reduce risk without active functioning of any device
- **Active** - Engineering controls
- **Procedural** - Administrative controls



Generally  
More  
Reliable /  
Effective









## Process Safety Overview

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5. Taking advantage of past experience





## Taking advantage of past experience


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*“Those who cannot remember the past are condemned to repeat it.” - George Santayana*

- Learnings from past (usually bad) experiences have been embodied in various forms:
 

– Regulations	– Handbooks
– Codes	– Guidelines
– Industry standards	– Procedures
– Company standards	– Checklists
– “Best practices”	– Supplier Recommendations





## Taking advantage of past experience

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- One term commonly used for non-regulatory codes and standards is “**RAGAGEPs**”
- From U.S. OSHA’s Process Safety Management Standard (Process Safety Information element):
 

29 CFR 1910.119(d)(3)(ii) The employer shall document that equipment complies with **recognized and generally accepted good engineering practices**.



## Taking advantage of past experience

- One term commonly used for non-regulatory codes and standards is “**RAGAGEPs**”
- From U.S. OSHA’s Process Safety Management Standard (Process Safety Information element)
- **Example:** International consensus standard IEC 61511 [ANSI/ISA-84.00.01 (IEC 61511 Mod)], “Functional Safety: Safety Instrumented Systems for the Process Industry Sector”



## RAGAGEPs

### *Recognized and Generally Accepted Good Engineering Practices*

- Take advantage of wealth of experience
- Pass on accumulated knowledge
- Reduce recurrence of past incidents
- Enable uniformity of expectations
- Reduce liabilities when followed



## Example: Anhydrous ammonia

- **Regulatory requirements:**  
E.g., U.S. OSHA Standard 29 CFR 1910.111, “Storage and Handling of Anhydrous Ammonia”
- **Industry standards**
  - CGA G-2, “Anhydrous Ammonia”
  - ANSI/CGA K61.1, “American National Standard Safety Requirements for the Storage and Handling of Anhydrous Ammonia”
- **Other standards apply to specific applications, e.g., EN 378 for ammonia refrigeration**



## RAGAGEPs Alphabet Soup

- |        |                      |
|--------|----------------------|
| • IEC  | • ASHRAE             |
| • NFPA | • IIAR               |
| • ASME | • ASTM               |
| • ISA  | • API                |
| • UL   | • AIChE/CCPS         |
| • FM   | • IRI                |
| • CGA  | • Chlorine Institute |
| • BS   | • SOCMA              |
| • DIN  | • etc.               |





## DISCUSSION

With what **RAGAGEPs** are you most familiar?

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## Process Safety Overview

1. What is *process safety*?
2. Opposite of process safety: Major incidents
3. The basic anatomy of process safety incidents
4. Overview of process safety strategies
5. Taking advantage of past experience
6. **Defense in depth / layers of protection**

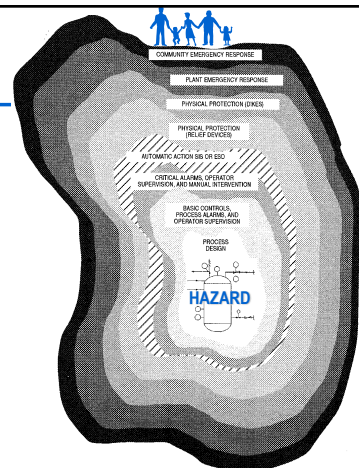


## Defense in depth / Layers of protection

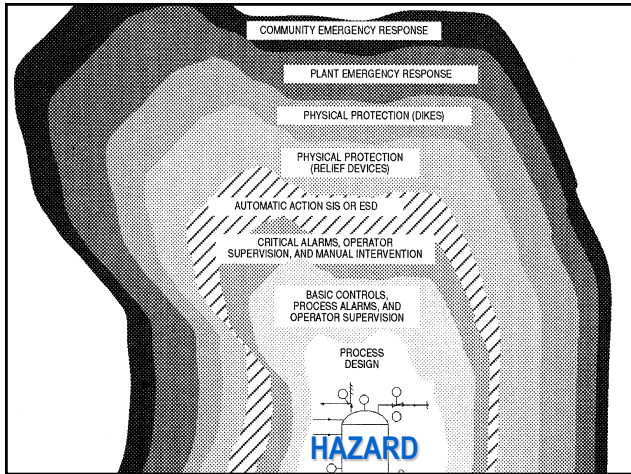
- Also called “Safety layers”
- Multiple layers may be needed, since no protection is 100% reliable
- Each layer must be designed to be effective
- Each layer must be maintained to be effective
- Some layers of protection are *contain and control measures*
- Other layers of protection are *safeguards*



“Layers of protection”  
between  
hazards and  
receptors  
=  
“Defense in depth”









### Defense in depth / Layers of protection

- Also called “Safety Layers”
- Multiple layers may be needed, since no protection is 100% reliable
- Each layer must be designed to be effective
- Each layer must be maintained to be effective
- Some layers of protection are **contain and control measures**
- Other layers of protection are **safeguards**



### Contain & control

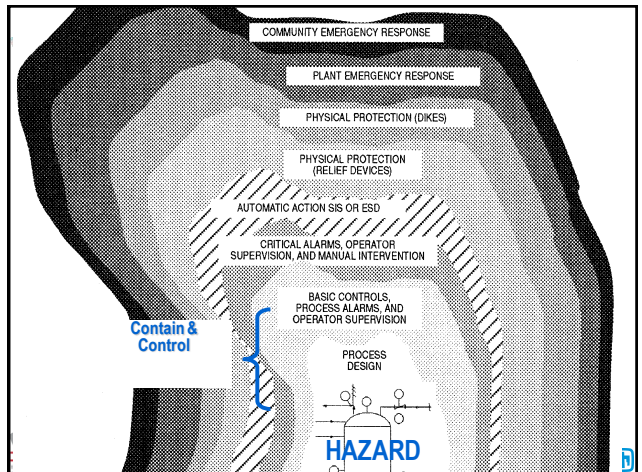
**Operational Mode: Normal operation**


**Objective: Maintain normal operation; keep hazards contained and controlled**

**Examples of *Contain & control* measures:**

- Basic process control system
- Inspections, tests, maintenance
- Operator training
  - How to conduct a procedure or operate a process correctly and consistently
  - How to keep process within established limits
- Guards, barriers against external forces
- Management of change





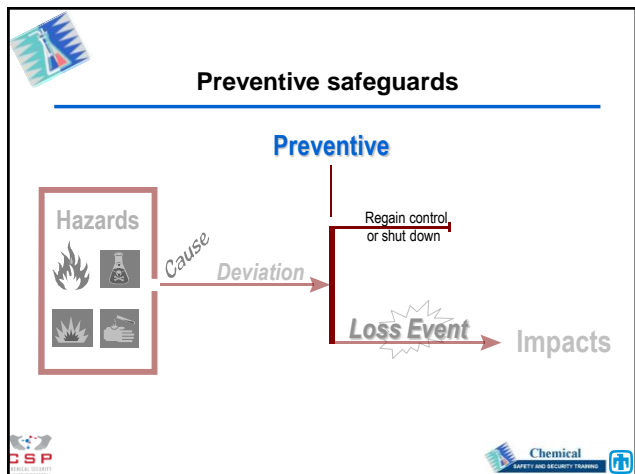
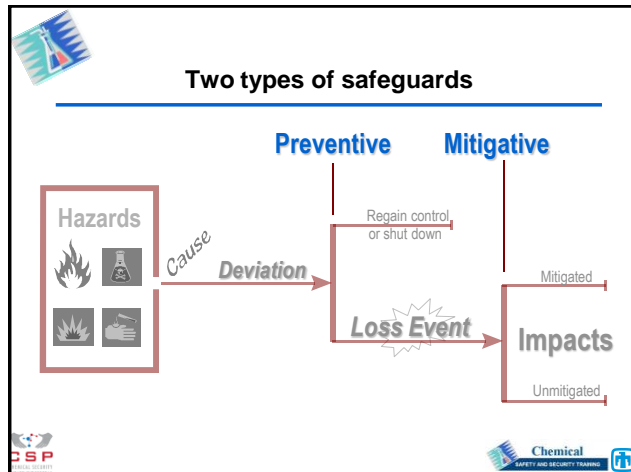



## Key definition

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**Safeguard:**  
*Any device, system, or action that would likely interrupt the chain of events following an initiating cause or that would mitigate loss event impacts.*

– CCPS 2008a Glossary

## Preventive safeguards



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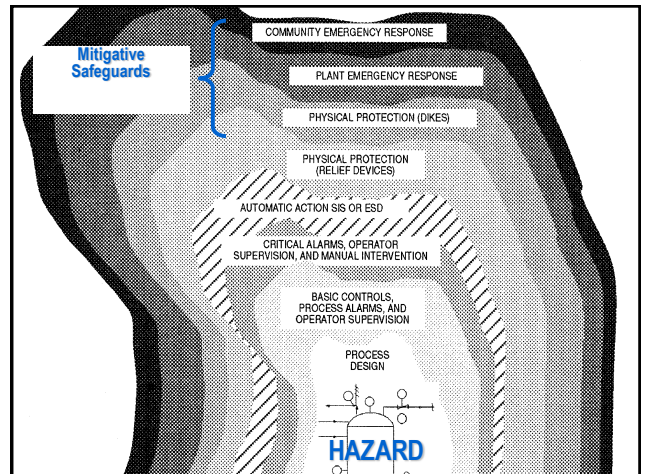
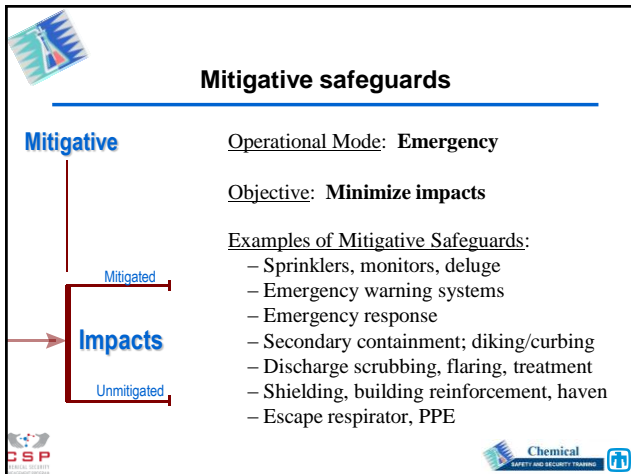
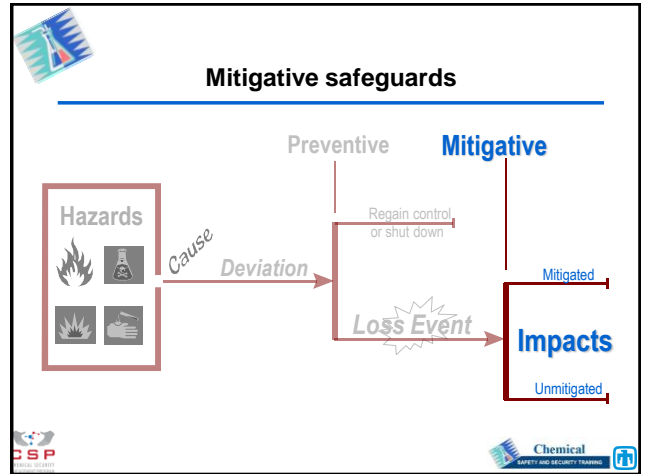
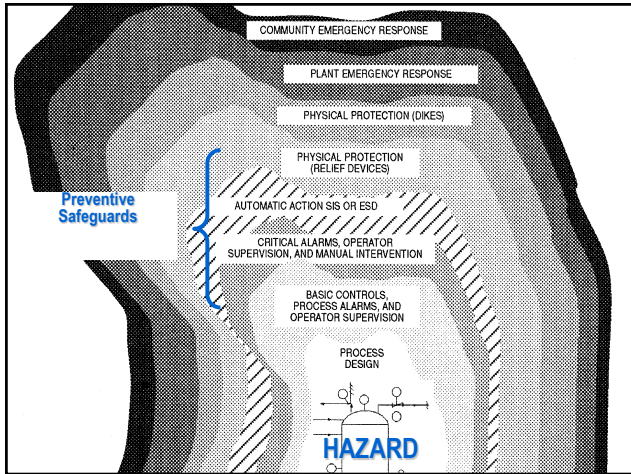
**Operational Mode:** Abnormal operation

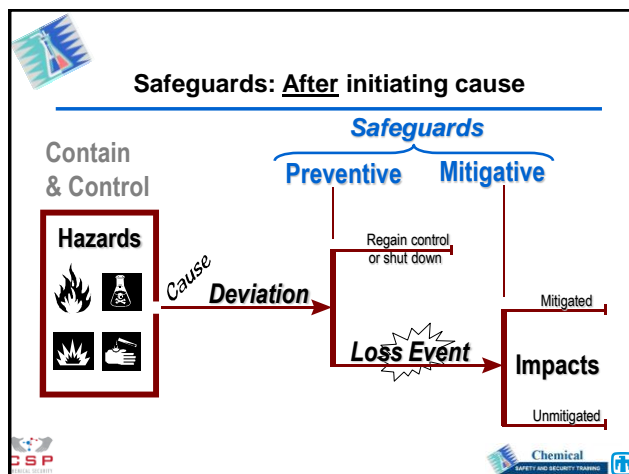
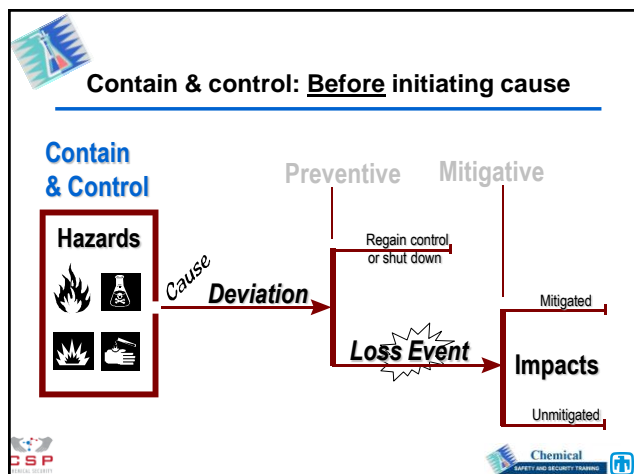
**Objective:** Regain control or shut down; keep loss events from happening

**Examples of Preventive Safeguards:**

- Operator response to alarm
- Safety Instrumented System
- Hardwired interlock
- Last-resort dump, quench, blowdown
- Emergency relief system





### Process Safety Overview

1. What is *process safety*?
2. Opposite of process safety: Major incidents
3. The basic anatomy of process safety incidents
4. Overview of process safety strategies
5. Taking advantage of past experience
6. Defense in depth / layers of protection
7. Elements of process safety management

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### Elements of a comprehensive PSM program

- Management systems
- Employee participation
- Process safety information
- Process hazard analysis
- Operating procedures
- Training
- Contractor safety
- Pre-startup safety reviews
- Mechanical integrity
- Safe work practices
- Management of change
- Emergency planning and response
- Incident investigation
- Compliance audits

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### *PSM elements addressed in this course*

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- Management systems
- Employee participation
- Process safety information
- **Process hazard analysis**
- Operating procedures
- Training
- Contractor safety
- **Pre-startup safety reviews**
- **Mechanical integrity**
- **Safe work practices**
- **Management of change**
- **Emergency planning and response**
- **Incident investigation**
- **Compliance audits**



### DISCUSSION

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What **PSM elements** do you find the most difficult to understand?  
... the most challenging to implement?

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